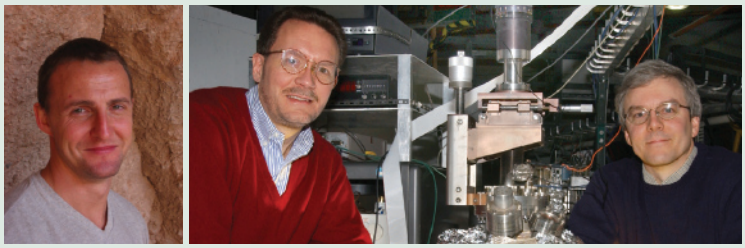
Palladium M_4-Valence-Valence and M_5-Valence-Valence Auger Spectra Determined by Auger-Photoelectron Coincidence Spectroscopy

M.T. Butterfield[1], R.A. Bartynski[1], and S.L. Hulbert[2]

[1]Department of Physics and Astronomy, Rutgers University; [2]National Synchrotron Light Source, Brookhaven National Laboratory

One of the best ways to probe electron correlations in the valence band of solids is to compare spectra of Auger decay processes with the predictions of various theories. But Auger spectra associated with different core levels are often closely spaced in energy and cannot be resolved by conventional means. Scientists from the NSLS and Rutgers University have recently succeeded in isolating the overlapping M_4-valence-valence and M_5-valence-valence Auger spectra of palladium metal by using vacuum ultraviolet synchrotron radiation from NSLS beamline U16B and a novel end station with two electron energy analyzers.



Authors (from left): Martin Butterfield, Robert Bartynski, and Steven Hulbert

One common way to probe the electronic structure of transition metals is through a mechanism called the Auger effect, which works as follows: An electron from a core electronic shell inside a metal atom is ejected by incoming radiation, leaving a vacant site, or hole, which is subsequently filled by another electron coming from a valence electronic shell (of higher energy than the core shell). By jumping into the hole, this second electron loses energy, which is then used to eject a third electron from another valence shell, called an Auger electron (**Figure 1**). Scientists can count the Auger electrons ejected as a function of their kinetic energy, called the Auger electron spectrum, which provides information on the correlations between the two holes left in the valence shell by the second and third electrons.

The kinetic energy distribution of Auger electrons, called the Auger line shape, is well understood when the electron-electron correlation energies in the valence band are either very large or very small. But palladium is an intermediate case that can test the ability to interpolate between these two extremes. Although an atom of palladium is an open-shell system (its outermost electronic shells are completely filled with electrons) in the solid form, it is missing only a fraction of an electron: It does not have a $4d^9$ but actually a $4d^{9+}$ configuration. So, palladium has what is called a marginally open shell. Thus, palladium should provide an interesting test of how theories formulated to explain the electronic properties of systems with totally filled, or closed, electronic shells can provide an accurate description of systems with marginally open shells.

Auger line shapes can be used to probe electron correlations in the valence band by comparing the measured Auger profiles against the prediction of various theories. But Auger spectra associated with different core levels are often closely spaced in energy and cannot be resolved by conventional means. With a technique called Auger-photoelectron coincidence spectroscopy, we have succeeded in distinguishing overlapping Auger spectra with different origins.

BEAMLINE
U16B

Funding
U.S. Department of Energy; National Science Foundation

Publication
M.T. Butterfield et al., "Pd M_{45} Auger Spectrum Determined by Auger-Photoelectron Coincidence Spectroscopy: Intrinsic Line Shape and Coster-Kroning Transitions," *Phys. Rev. B.*, 66, 115115 (2002).

Contact information
Steven Hulbert, NSLS, Brookhaven National Laboratory, Upton, NY

Email: hulbert1@bnl.gov

The importance of correlation effects in core-valence-valence Auger spectra can be quantified by the ratio of the Coulomb repulsion energy to the bandwidth, which, in transition metals, is usually the width of the *d* bands. If this quantity is small, the shape of the Auger spectrum will be band-like. In contrast, if this quantity is large, the lineshape will be atomic-like. Cini and Sawatzky independently developed a theoretical model of Auger transitions that describes the Auger line shape intermediate between these two extremes.

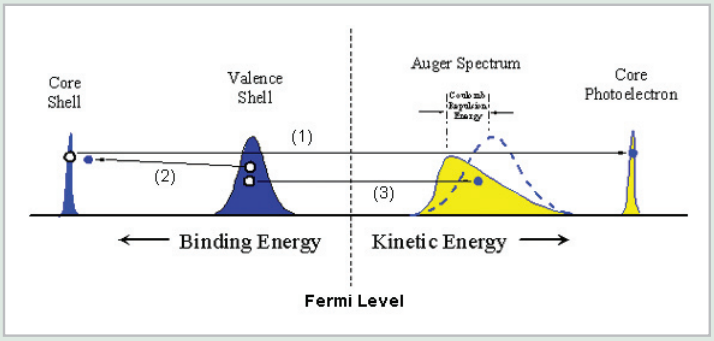


Figure 1. Energy level diagram for the Auger decay process. An electron in the core electronic shell is ejected (1) by a synchrotron soft x-ray and then an electron from the valence band fills (2) the hole previously occupied by the first electron. The energy released by this transition is transferred to the emission (3) of another valence electron, called an Auger electron. The Auger electron is produced by what is called core-valence-valence Auger decay. If the valence electrons are correlated via a Coulomb repulsion energy, the lineshape of the Auger spectrum can change shape as shown.

For palladium, the Cini-Sawatzky model cannot provide a complete description of our measured Auger spectra. We have succeeded in matching the entire Auger spectra by using an extension of the Cini-Sawatzky theory in which each electronic multiplet of the two-hole final state can be considered as having its own value of the Coulomb repulsion energy, so each will experience a different amount of distortion. The result of a fit using this approach is shown in **Figure 2**.

In the M_4-valence-valence Auger spectrum, we notice that excess emission above the theoretical curve accounts for a larger fraction of the spectrum than in the M_5-valence-valence line. This additional M_4 emission is attributed to a Coster-Kronig transition, whereby the palladium M_4 core hole is filled by an M_5 core electron, and then the remaining M_4 hole decays. We have recently found that the Coster-Kronig channel is dramatically enhanced in surface alloys of palladium and silver.

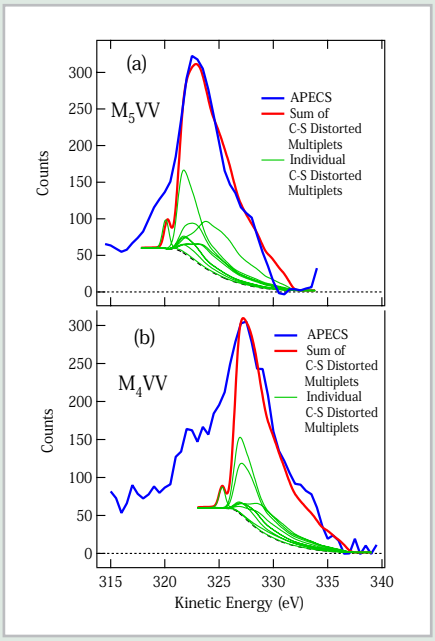


Figure 2. (a) Palladium M_4 valence-valence and (b) palladium M_5 valence-valence Auger spectra (blue curves) along with the individual (green curves) and the sum of the Cini-Sawatzky distorted final state multiplets (red curve) added to a simple inelastic background (black curve).